



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/09740 <b>(22) International Filing Date:</b> 4 May 1999 (04.05.99) <b>(30) Priority Data:</b> 09/073,148                      5 May 1998 (05.05.98)                      US <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). <b>(72) Inventors:</b> CHEN, Tan-Jen; 5615 Lofty Magnolia Court, Kingwood, TX 77345 (US). DAVIS, S., Mark; 6160 Wildlife Way Court, Baton Rouge, LA 70817 (US). MARTENS, Luc, R., M.; Prinsenbeemdlaan 3, B-1860 Meise (BE). JANSSEN, Marcel, J., G.; Domeinstraat 84, B-3010 Kessel-Lo (BE). RUZISKA, Philip, A.; 2010 Wind Creek Drive, Kingwood, TX 77345 (US). <b>(74) Agents:</b> ZBORAY, James, A. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> HYDROCARBON CONVERSION TO PROPYLENE  <b>(57) Abstract</b>  The invention provides a method for converting an olefinic hydrocarbon feedstock to propylene comprising: contacting a hydrocarbon feedstock under catalytic cracking conditions with a catalyst comprising a catalyst selected from the group consisting of SAPO catalysts, MeAPO catalysts, MeASPO catalysts, ELAPO catalysts, ELASPO catalysts, rare earth exchanged catalysts from any of the preceding groups, and mixtures thereof, under cracking conditions to selectively produce propylene. The invention further provides a method for stabilizing a catalyst to steam from the foregoing group by ion exchange with a rare earth metal. A catalyst has enhanced stability as used herein when treated with a rare earth metal or metals in a concentration effective to provide a catalyst which exhibits a higher conversion of a hydrocarbon feedstock to propylene than does an equal quantity of an untreated sample of the same catalyst under the same conditions following exposure of each catalyst to steam for a period of at least 10 hours.		

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## HYDROCARBON CONVERSION TO PROPYLENE

### FIELD OF THE INVENTION

The invention relates to catalytic cracking of hydrocarbons. Particularly the invention relates to a method providing improved selectivity for cracking hydrocarbon feedstocks to propylene by contacting the hydrocarbon under cracking conditions with a catalyst selected from the non-zeolitic molecular sieves consisting of silicoaluminophosphates ("SAPO"), metal aluminophosphates ("MeAPO"), metal aluminosilicophosphates ("MeASPO"), elemental aluminophosphates ("ElAPO") and elemental aluminosilicophosphates ("ElASPO") where the metals include divalent Co, Fe, Mg, Mn, and Zn and trivalent Fe and the elements include Li, Be, B, Ga, Ge, As, and Ti.

### BACKGROUND OF THE INVENTION

Thermal and catalytic conversion of hydrocarbons to olefins is an important industrial process producing millions of pounds of olefins each year. Because of the large volume of production, small improvements in operating efficiency translate into significant profits. Catalysts play an important role in more selective conversion of hydrocarbons to olefins.

While important catalysts are found among the natural and synthetic zeolites, it has also been recognized that non-zeolitic molecular sieves such as silicoaluminophosphates (SAPO) including those described in U. S. Patent 4,440,871 also provide excellent catalysts for cracking to selectively produce light hydrocarbons and olefins. The SAPO molecular sieve has a network of  $\text{AlO}_4$ ,  $\text{SiO}_4$ , and  $\text{PO}_4$  tetrahedra linked by oxygen atoms. The negative charge in the network is balanced by the inclusion of exchangeable protons or cations such as alkali or alkaline earth metal ions. The interstitial spaces or channels formed by the crystalline network enables SAPOs to be used as molecular sieves in separation processes and in catalysis. There are a large number of known SAPO

structures. The synthesis and catalytic activity of the SAPO catalysts are disclosed in U. S. Patent 4,440,871.

In other crystalline microporous solids belonging to the class of aluminophosphates the framework is normally neutral (Al (III) :P (V) atomic ratio = 1). This framework can be made negative and thereby gives these materials advantageous properties such as adsorption, cation exchange or catalytic activity by replacing P(V) or the pair Al (III), P(V) with a tetravalent element such as silicon, converting to the closely related SAPO structure discussed above, or by replacing Al (III) with a metal, especially a divalent metal such as zinc or cobalt, the materials obtained being denoted by the acronym MeAPO where Me is the metal, or else by combining these two types of substitution, the materials obtained being denoted by the acronym MeAPSO. A group of such materials is described in U. S. Patent 5,675,050.

In the International Application WO 91/18851 the exchange of cations to provide Lewis acid sites in zeolite and SAPO catalytic structures in isomerization catalysts is disclosed. SAPO-11 is disclosed as being particularly effective in this system. The application focuses on skeletal isomerization of n-olefins. There is no teaching of enhanced selectivity or stability under catalytic cracking conditions. Nor is there any discussion of increased stability in rare earth exchanged SAPO.

SAPO catalysts mixed with zeolites (including rare earth exchanged zeolites) are known to be useful in cracking of gasoils (U. S. Patent 5,318,696). U. S. Patents 5,456,821 and 5,366,948 describe cracking catalysts with enhanced propylene selectivity which are mixtures of phosphorus treated zeolites with a second catalyst which may be a SAPO or a rare earth exchanged zeolite. Rare earth treated zeolite catalysts useful in catalytic cracking are disclosed in U. S. Patents 5,380,690, 5,358,918, 5,326,465, 5,232,675 and 4,980,053. The use of SAPO catalysts for cracking crude oil feed or "carbon-hydrogen fragmentation compounds" (materials with 5 or less carbons) is disclosed in U. S. Patent

4,666,875 and 4,842,714 (SAPO-37 preferred for cracking gas oils). Although these patents disclose the use of rare earth exchanged SAPO catalysts, they state: "At present the presence of rare earth cations with the SAPO molecular sieves has not been observed to be beneficial to the activity of the SAPO component. The exact nature of the relationship of multi-valent cations and SAPO catalysts is not clearly understood at present, although in some instances their presence may be beneficial." (U. S. Patent 4,666,875 at Col. 4 Lines 39-44, U. S. Patent 4,842,714 Col. 11, Lines 29-34.)

The art has not previously recognized the highly selective conversion of hydrocarbon, especially naphtha feedstocks to propylene promoted by SAPO and related catalysts nor the improved stability obtained by rare earth exchanging such catalysts.

### SUMMARY OF THE INVENTION

The invention provides a method for converting an olefinic hydrocarbon feedstock to propylene comprising: contacting a hydrocarbon feedstock under catalytic cracking conditions with a catalyst comprising a nonzeolitic catalyst selected from the group consisting of SAPO catalysts, MeAPO catalysts, MeASPO catalysts, ElAPO catalysts, ElASPO catalysts, rare earth exchanged catalysts from any of the preceding groups, and mixtures thereof, under cracking conditions to selectively produce propylene. Preferably the method is carried out to produce propylene in a propylene to ethylene ratio of at least 4:1 and a propylene to butylene ration of at least 2:1. The invention further provides an method for stabilizing a catalyst from the foregoing group by ion exchange with a rare earth metal. A catalyst has enhanced stability as used herein when treated with a rare earth metal or metals in a concentration effective to provide a catalyst which exhibits a higher conversion of a hydrocarbon feedstock to propylene than does an equal quantity of an untreated sample of the same catalyst under the same conditions following exposure of each catalyst to steam for a period of at least 10 hours. The invention also provides an improvement in methods for catalytic

cracking of an olefinic hydrocarbon feedstock to produce a light olefin containing product wherein it is desired to improve the propylene content of the product mixture. The improvement comprises mixing a catalyst selected from the non zeolitic catalyst group consisting of SAPO catalysts, MeAPO catalysts, MeASPO catalysts, ElAPO catalysts and ElASPO catalysts with a second cracking catalyst in a quantity sufficient to increase propylene content in the light olefin product while decreasing either ethylene or butylene when the product composition obtained with the mixed catalyst is compared to the product composition obtained with the second catalyst alone under the same reaction conditions.

## 10 DETAILED DESCRIPTION OF THE INVENTION

The silicoaluminophosphate (SAPO) catalysts useful in the present invention have a three-dimensional microporous crystal framework structure of  $\text{PO}_2^+$ ,  $\text{AlO}_2^-$  and  $\text{SiO}_2$  tetrahedral units, and whose essential empirical chemical composition on an anhydrous basis is:  $m \text{ R}:(\text{Si}[x]\text{Al}[y]\text{P}[z])\text{O}[2]$  wherein "R" represents at least one organic templating agent present in the intracrystalline pore system: "m" represents the moles of "R" present per mole of  $(\text{Si}[x]\text{Al}[y]\text{P}[z])\text{O}_2$  and has a value of from zero to 0.3, the maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular silicoaluminophosphate species involved, "x", "y" and "z" represent the mole fractions of silicon, aluminum and phosphorus, respectively, present as tetrahedral oxides, representing the following values for "x", "y" and "z".

## Mole Fraction

x	y	z
0.01	0.47	0.52
0.94	0.01	0.05
0.98	0.01	0.01
0.39	0.60	0.01
0.01	0.60	0.39

5

When synthesized in accordance with the process disclosed in U. S. Patent 4,440,871, the minimum value of "m" in the formula above is 0.02. In a preferred sub-class of the SAPOs useful in this invention, the values of "x", "y" and "z" in the formula above are set out in the following table:

10

## Mole Fraction

	x	y	z
	0.02	0.49	0.49
	0.25	0.37	0.38
5	0.25	0.48	0.27
	0.13	0.60	0.27
	0.02	0.60	0.38

Preferred SAPO catalysts include SAPO-11, SAPO-17, SAPO-31, SAPO-34, SAPO-35, SAPO-41, and SAPO-44.

10        The catalysts suitable for use in the present invention include, in addition to the SAPO catalysts, the metal integrated aluminophosphates (MeAPO and ELAPO) and metal integrated silicoaluminophosphates (MeAPSO and ElAPSO). The MeAPO, MeAPSO, ELAPO, and ElAPSO families have additional elements included in their framework. For example, Me represents the elements Co, Fe,  
 15    Mg, Mn, or Zn, and El represents the elements Li, Be, Ga, Ge, As, or Ti. Preferred catalysts include MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11, MeAPSO-31, and MeAPSO-41, MeAPSO-46, ELAPO-11, ELAPO-31, ELAPO-41, ElAPSO-11, ElAPSO-31, and ElAPSO-41.

20        The non-zeolitic SAPO, MeAPO, MeAPSO, ELAPO and ElAPSO classes of microporous materials are further described in the "Atlas of Zeolite Structure Types" by W. M. Meier, D. H. Olson and C. Baerlocher (4th ed., Butterworths/Intl. Zeolite Assoc. (1996) and "Introduction to Zeolite Science and Practice", H. Van Bekkum, E.M. Flanigen and J.C. Jansen Eds., Elsevier, New York, (1991)).

25        The selected catalysts may also include cations selected from the group consisting of cations of Group IIA, Group IIIA, Groups IIIB to VIIB and rare earth cations selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium,



terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and mixtures thereof.

Preferred olefinic hydrocarbon feedstocks are naphthas in the boiling range of 18° to 220°C (65°F to 430°F). The naphthas may be thermally cracked  
5 naphthas or catalytically cracked naphthas. The feed should contain from at least 10 wt% to about 70 wt% olefins, preferably 20 wt% to 70 wt%, and may also include naphthenes and aromatics. The naphthas may contain paraffins in the range of 5 wt % to 35 wt%, preferably 10 wt% to 30 wt %, most preferably 10  
10 wt% to 25 wt%. For example, the naphtha may be derived from fluid catalytic cracking ("FCC") of gas oils and resids, or from delayed or fluid coking of resids. The preferred naphtha streams are derived from FCC gas oils or resids which are typically rich in olefins and diolefins and relatively lean in paraffins.

Catalytic cracking conditions means a catalyst contacting temperature in the range of about 400°C to 750°C, more preferably in the range of 450°C to  
15 700°C, most preferably in the range of 500°C to 650°C. The catalyst contacting process is preferably carried out at a weight hourly space velocity (WHSV) in the range of about 0.1 Hr<sup>-1</sup> to about 300 Hr<sup>-1</sup>, more preferably in the range of about 1.0 Hr<sup>-1</sup> to about 250 Hr<sup>-1</sup>, and most preferably in the range of about 10 Hr<sup>-1</sup> to about 100 Hr<sup>-1</sup>. Pressure in the contact zone may be from 0.1 to 30 atm. absolute,  
20 preferably 1 to 3 atm. absolute, most preferably about 1 atm. absolute. The catalyst may be contacted in any reaction zone such as a fixed bed, a moving bed, a slurry, a transfer line, a riser reactor or a fluidized bed.

### Test Conditions

A series of runs in a small bench reactor was conducted on hexene as a  
25 model compound. Comparison runs with a ZSM-5 zeolite catalyst commercially available from Intercat. Inc., of Sea Girt, New Jersey were conducted over a fixed bed of catalyst. The effluent stream was analyzed by on-line gas chromatography. A column having a length of 60 m packed with fused silica was used for the analysis. The gas chromatograph was a dual flame ionization detector

equipped Hewlett-Packard Model 5880. All tabulated data is in weight per cent unless otherwise indicated.

### Example 1 Constant Reactor Conditions

The hexene model compound was cracked over ZSM-5, SAPO-11 and  
5 SAPO-34 catalysts at 650°C, 12 hr<sup>-1</sup> WHSV, 1.6 nitrogen dilution, 12 psig.

Table 1			
Catalyst	ZSM-5	SAPO-34	SAPO-11
Conversion	95.4	63.6	88.8
<b>Key Results</b>			
Ethylene	24.5	11.0	8.4
Propylene	35.8	30.3	54.8
Butylenes	12.8	11.2	11.8
Aromatics	12.8	2.7	8.5
Light Saturates	9.5	8.5	5.4
<b>Selectivity</b>			
<b>(% of Conversion)</b>			
Ethylene	25.7	17.3	9.5
Propylene	37.5	47.6	61.7
Butylene	13.4	17.6	13.3
Propylene/ethylene	1.5	2.8	6.5
Propylene/butylene	2.8	2.7	4.7

As can be seen from Table 1, the SAPO-11 catalyst was slightly less active than the comparison ZSM-5 in terms of conversion. The data show that SAPO-11 was more selective for propylene over ethylene and butylene as ZSM-5, and SAPO-34  
10 also shows significantly increased production of propylene over both ethylene and butylene.

**Example 2 Constant Conversion**

In this example the conditions are the same as in Example 1 except the weight hourly space velocity was adjusted to make conversion equal for the control ZSM-5 and SAPO-11.

Table 2		
Catalyst	ZSM-5	SAPO-11
WHSV, Hr <sup>-1</sup>	40	12
Conversion	89.0	88.8
<b>Key Results</b>		
Ethylene	13.1	8.4
Propylene	47.6	54.8
Butylene	14.9	11.8
Aromatics	7.4	8.5
Light Saturates	6.1	5.4
<b>Selectivity</b>		
Ethylene	14.7	9.5
Propylene	53.3	61.7
Butylene	16.7	13.3
Propylene/Ethylene Ratio	3.6	6.5
Propylene/Butylene Ratio	3.2	4.7

5

As can be seen from Table 2, SAPO-11 produced significantly more propylene and less ethylene and butylenes than ZSM-5 catalyst.

**Example 3 Effect of Temperature and Throughput**

In this example SAPO-11 extrudate catalyst was tested with the hexene model compound in the apparatus of Example 1 under the conditions indicated in Table 3.

Table 3			
Temperature, °C	650	600	600
WHSV, Hr <sup>-1</sup>	12	12	8
Conversion	88.8	75.9	87.9
<b>Key Results</b>			
Ethylene	8.4	3.6	3.9
Propylene	54.8	60.6	69.7
Butylene	11.8	7.1	7.4
Aromatics	8.5	2.7	5.0
Light Saturates	5.4	1.8	2.0
<b>Selectivity, %</b>			
Ethylene	9.5	4.7	4.4
Propylene	61.7	79.8	79.3
Butylene	13.3	9.4	8.4
Propylene/Ethylene Ratio	6.5	16.8	17.9
Propylene/Butylene Ratio	4.7	8.5	9.4

- 5 As the data above indicate, selectivity is improved by reducing the temperature and by maintaining high conversion by decreasing throughput thus increasing the average time the feedstock is in contact with the catalyst. The propylene/ethylene ratio approaching 18:1 is exceptional as is the propylene/butylene ratio at 9.4:1. With ZSM-5 catalysts lowering the temperature typically results in increasing
- 10 butylene selectivity, while the SAPO catalysts display the opposite trend which is unexpected. It has been found that the selectivity of the catalysts can be

maintained over a wide range of conversion levels so long as cracking conditions are maintained.

#### Example 4 Selectivity in Cracking of a Typical Refinery Feedstock

5 A typical refinery feedstock, Baton Rouge Light Cat. Naphtha, (LCN) was contacted with fresh and steamed SAPO-11 at 600°C, 6 Hr<sup>-1</sup> WHSV, 1.6 N<sub>2</sub> dilution, and 12 psig. The results are listed in Table 4.

Table 4			
Catalyst	ZSM-5	SAPO-11	SAPO-11
Presteamming Conditions	816°C/40 Hr.	Fresh	593°C/16 Hr.
Conversion	40.7	33.9	33.2
<b>Key Results</b>			
Ethylene	5.1	3.2	2.6
Propylene	24.7	24.9	25.3
Butylene	9.5	4.2	3.8
Aromatics	4.5	5.5	4.4
Light Saturates	1.4	1.6	1.5
<b>Selectivity, %</b>			
Ethylene	12.5	9.4	7.8
Propylene	60.7	73.5	76.2
Butylenes	23.3	12.4	11.4
Propylene/Ethylene Ratio	4.8	7.8	9.7
Propylene/Butylene Ratio	2.6	5.9	6.6

The selectivity observed with the model compound is maintained with the refinery feedstock. Selectivity appears to improve when the catalyst is pre-steamed.

10

**Example 5 Performance of Calcium exchanged SAPO-11**

To 10 g SAPO-11 was added 1000 ml of a 10 wt%  $\text{Ca}(\text{NO}_3)_2$  solution. This solution was stirred for 16 hrs at 65°C. After washing, the sample was dried overnight at 90°C, followed by air calcination for 16 hrs at 525°C. The procedure  
5 was repeated twice to obtain the finished catalyst. The calcium exchanged SAPO-11 was contacted with the hexene model compound at 600°C, and 2 Hr<sup>-1</sup>. The nitrogen diluent to hydrocarbon ratio was 5:1. The results are shown in Table 5.

Table 5		
Catalyst	ZSM-5	SAPO-11
Conversion	99.3	89.8
Key Results		
Ethylene	20.4	4.3
Propylene	22.6	57.5
Butylenes	8.3	11.8
Aromatics	25.0	1.4
Selectivity, %		
Ethylene	20.5	4.8
Propylene	22.8	64.0
Butylenes	8.4	13.1
Propylene/Ethylene Ratio	1.1	13.4
Propylene/Butylene Ratio	2.7	2.9

10 As demonstrated by the data above Ca SAPO-11 was found to be very selective for propylene with a propylene selectivity of 64% and low production of both ethylene and butylenes. An additional benefit is the low aromatics production of only 1.4%

**Example 6 Improved Stability with Rare Earth Treated Nonzeolitic Catalyst**

SAPO-11 treated with a rare earth (lanthanum) resists loss of activity when subjected to prolonged exposure to steam. Most zeolite and other molecular sieve catalysts display a characteristic loss of activity when exposed to steam over a prolonged period. As the data below demonstrate rare earth treatment of catalyst (SAPO-11) produces a catalyst with 60-70% improvement in catalyst activity relative to non-treated SAPO-11 while retaining the outstanding selectivity for propylene over both ethylene and butylene observed in the examples above. A sample of SAPO-11 was ion-exchanged with a lanthanum solution by suspending 10 grams of SAPO-11 in 100 grams of water and 5 grams of  $\text{LaCl}_3 \cdot 6 \text{H}_2\text{O}$  were added. The mixture was refluxed at 100°C for 4 hrs, then dried and calcined.

The exchanged catalyst was contacted with Baton Rouge Light Cat Naphtha, at 500°C, 1/1 steam to hydrocarbon weight ratio, at 5  $\text{Hr}^{-1}$ , 12 psig in the apparatus of Example 1. The steamed catalysts were treated at 760°C with 100% steam for 16 hours prior to the cracking test. The results are shown in Table 6 below.

Table 6			
Catalyst	Fresh SAPO-11	Steamed SAPO- 11	Steamed LaSAPO- 11
Conversion	27.5	12.0	20.2
<b>Key Results</b>			
Ethylene	1.5	0.4	0.9
Propylene	23.1	10.0	17.0
Butylene	2.7	1.5	2.1
Aromatics	2.9	2.1	2.7
Light Saturates			
<b>Selectivity, %</b>			
Ethylene	5.5	3.3	4.4
Propylene	84.0	83.1	84.0
Butylene	9.8	12.5	10.4
Propylene/Ethylene Ratio	15.2	25.2	19.1
Propylene/Butylenes Ratio	8.5	6.6	8.1

The preceding data show a positive result of rare earth treatment of a SAPO catalyst. The improved resistance to loss of activity on exposure to steam allows prolonged use of the catalyst. The foregoing results are provided to illustrate the operation of the invention in some of its embodiments. The examples are provided by way of illustration and not as limitations on the scope or practice of the invention, which is defined and limited by the following claims.



CLAIMS

We claim:

1. A method of converting an olefinic hydrocarbon feedstock to a high propylene content product comprising: contacting a hydrocarbon feedstock  
5 under catalytic cracking conditions with a catalyst comprising a catalyst selected from the group consisting of SAPO catalysts, MeAPO catalysts, MeASPO catalysts, ElAPO catalysts and ElASPO catalysts, under cracking conditions to selectively produce propylene.
- 10 2. In a method for catalytic cracking of an olefinic hydrocarbon feed to produce a light olefin containing product, the improvement which comprises mixing a catalyst selected from the non zeolitic catalyst group consisting of SAPO catalysts, MeAPO catalysts, MeASPO catalysts, ElAPO catalysts and ElASPO catalysts with a second cracking catalyst in a  
15 quantity sufficient to increase propylene content in the light olefin product while decreasing either ethylene or butylene when the product composition obtained with the mixed catalyst is compared to the product composition obtained with the second catalyst alone under the same reaction conditions.
- 20 3. A method for enhancing the stability of a silicoaluminophosphate catalyst in propylene production which comprises ion exchanging the catalyst with a solution which comprises a rare earth metal.
4. A method for producing propylene in a cracking process while minimizing production of butylene which comprises contacting an olefinic hydrocarbon feed with a non-zeolitic silicoaluminophosphate containing catalyst under  
25 cracking conditions to produce at least 2 times as much propylene as butylenes.

5. A method for producing propylene in a cracking process while minimizing production of ethylene which comprises contacting an olefinic hydrocarbon feed with a non-zeolitic silicoaluminophosphate containing catalyst under cracking conditions to produce at least 2 times as much propylene as ethylene.  
5
6. The method of claim 1 wherein the selectivity produces a propylene to butylene ratio of at least 2:1 or a propylene to ethylene of at least 4:1.
7. The method of claim 1 or 2 wherein the olefinic hydrocarbon feedstock consists essentially of hydrocarbons boiling within the range of 18° to 220° C (65°F to 430°F).  
10
8. The method of claim 1 or 2 wherein the olefinic hydrocarbon feedstock consists essentially of hydrocarbons boiling in the range of 18° to 148°C (65°F to 300°F).
9. The method of claim 1 or 2 wherein the olefinic hydrocarbon feedstock comprises from 10 wt% to 70 wt% olefins.  
15
10. The method of claim 1 or 2 wherein the olefinic hydrocarbon feedstock comprises from 20 wt% to 70 wt% olefins.
11. The method of claim 1 or 2 wherein the olefinic hydrocarbon feedstock comprises from 5 wt% to 35 wt % paraffins.
12. The method of claim 1 or 2 wherein the olefinic hydrocarbon feedstock comprises from 10 wt% to 25 wt % paraffins.  
20
13. The method of claim 1 or 2 wherein the catalyst is contacted in the range of 400°C to 700°.
14. The method of claim 1 or 2 wherein the catalyst is contacted at a WHSV of 1 to 300 hr-1.  
25

15. The method of claim 1 or 2 wherein the catalyst is contacted at a pressure of 0.1 to 30 atm. absolute.
16. The method of claim 1 or 2 wherein the catalyst comprises a catalyst selected from the group consisting of SAPO-11, SAPO-17, SAPO-31, SAPO-34, SAPO-35, SAPO-41, SAPO-44, MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11, MeASPO-31, MeASPO-41, MeASPO-46, ElAPO-11, ElAPO-31, ElAPO-41, ElAPSO-11, ElAPSO-31 and ElASPO-41.
17. The method of claim 1 wherein the catalyst is prepared by a method which comprises ion exchanging the catalyst with a solution comprising an alkaline earth metal ion or a rare earth metal ion.
18. The method of claim 2 wherein the selected catalyst is prepared by a method which comprises ion exchanging the catalyst with an aqueous solution comprising an alkaline earth metal ion or a rare earth metal ion.
19. The method of claim 3, 17, or 18 wherein the catalyst is exchanged against a solution comprising a rare earth metal ion selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and mixtures thereof
20. The method of claim 19 wherein the rare earth metal ion comprises lanthanum.
21. The method in claim 1 or 2 wherein the hydrocarbon feed is cracked over the catalyst at reactor temperatures of from 400-700°C, pressures of from 0.1 atmosphere to 30 atmospheres absolute, and weight hourly space velocities of from 0.1 hr<sup>-1</sup> to 100 hr<sup>-1</sup>.

22. The method of claim 3, 4, or 5 wherein the catalyst is selected from the group consisting of SAPO catalysts, MeAPO catalysts, MeASPO catalysts, ElAPO catalysts and ElASPO catalysts and mixtures thereof.
- 5 23. A method according to claim 4 or 5 wherein the process produces at least 4 times as much propylene as ethylene.
24. A method according to claim 22 wherein the catalyst is a SAPO selected from the group consisting of SAPO-11, SAPO-17, SAPO-31, SAPO-34, SAPO-35, SAPO-41, SAPO-44.
- 10 25. A method according to claim 4 wherein at least 2.5 times as much propylene as butylenes is produced.
26. A method according to claim 4 or 5 wherein at least 3 times as much propylene as butylenes is produced.
27. A method according to claim 5 herein at least 2 times as much propylene as butylenes is produced.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/09740

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C4/06 C10G11/05 B01J29/84

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 395 345 A (ARCO CHEM TECH) 31 October 1990 (1990-10-31) ---	1,2,4-27
A	EP 0 142 154 A (UNION CARBIDE CORP) 22 May 1985 (1985-05-22) ---	1,2,4-27
A	EP 0 142 156 A (UNION CARBIDE CORP) 22 May 1985 (1985-05-22) ---	1,2,4-27
X	US 4 666 875 A (PELLET REGIS J ET AL) 19 May 1987 (1987-05-19) cited in the application column 9, line 12 - line 18; claim 1 -----	3,19,20, 22

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

13 September 1999

Date of mailing of the international search report

7. 09.99

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Janus, S

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/09740

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99 /09740

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1, 2, 4-18, 19-20(in part), 21, 22(in part), 23-27

Process for the selective preparation of propylene by conversion of an olefinic feedstock in the presence of a non-zeolitic silicoaluminophosphate catalyst.

2. Claims: 3, 19-20(in part), 22(in part)

Process for enhancing the stability of a silicoaluminophosphate catalyst in propylene production.



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/09740

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